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Vibrational transition probabilities of the bands of BO - α System.

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Franck-Condon factors have been computed by Bates' method (1949). These results have been used along with the already available experimental data from the work of Elliot (1933) to evaluate a relation between R_e, the electronic transition moment and r, the internuclear separation, in the form.

$$R_e(r) = \text{Constant}\ (1 - 0.4584r)$$

This relation has been used to obtain improved Franck-Condon factors.

Robinson & Nicholls (1960) have reported the value of coefficient ρ as 1.66. A check has been made on this value by using their data and we obtained the result as 0.3954 instead. It is shown that the coefficient 0.4584 gives a better approach towards theoretical values.

Introduction

The study of molecular spectra has been a powerful tool in the investigation of astrophysical problems. The recent improvements in the basic theoretical concepts have enhanced its importance.

The BO molecule is an astral molecule. The quantitative experimental data available from the old work of Elliot (1933) reproduced in table 1, is subjected to verification by theoretical study. The accuracy in the measurement of intensities as stated by Elliot is $\pm$ 5%. Intensity values of Robinson & Nicholls (1960) and of Elliot (1933) are nearly identical.

Theoretical Computations

Anharmonic wave-functions have been computed by treating the diatom as anharmonic oscillator. These in turn are used to evaluate the Franck-Condon factors. The numerical integration method of Bates (1949) is used for this purpose. The results of these calculations are provided in table 1. The constants from Herzberg's compilation are used in the computations.

TABLE 1

Band	Intensity	F.C. Factors	r-centroids
0,0	4.6	0.0386	1.275
0,1	9.2	0.1427	1.301
0,2	8.5	0.2443	1.328
0,3	6.0	—	1.357
1,0	9.5	0.1015	1.257
1,1	10.0	0.1683	1.241
1,2	3.8	0.1007	1.310
2,0	8.9	0.1586	1.241
2,1	4.4	0.1103	1.266
2,2	—	—	1.294
2,3	—	—	1.319

r-centroids

The r-centroids are essential for the study of variation of electronic transition moment. As it is the object of this work to take into account the contribution of electronic transition moment to the vibrational transition probability, r-centroids have been evaluated by the quadratic equation method of Nicholls & Jarmain (1956). The results are reproduced in table 1.

$R_e - r$ RELATION

r-centroids so obtained have been used along with the experimental intensity measures, to obtain the following relation between R_e and r. In the absence of theoretical method of obtaining a relation between R_e and r, the semi-empirical method due to Nicholls & Jarmain (1956) is used.

$$R_e(r) = \text{const.}\ (1 - 0.4584r)$$

Using the relation the Franck-Condon factors have been smoothed out. These results are listed in column 4 of table 2.

Table 2 shows the comparison of Franck-Condon factors with the experimental (I/ν^4) values, where I is the intensity and ν the band frequency. These quantities have been expressed in terms of the values for the first band in each progression. The ratios of I/ν^4 values with the Franck-Condon

factors for anharmonic oscillator are designated as δ_{AH} and those for the smoothed values as δ smoothed.

TABLE 2. TRANSITION PROBABILITIES BO - α SYSTEM

Progression	V''	δ_{AM}	δ smoothed (ρ=0.4583)	δ smoothed (ρ=0.3954)
V'=0	0	1	1	1
	1	0.9241	0.939	0.918
	2	0.6708	0.76	0.733
	3	0.7375	0.894	0.845
	4	0.775	1.01	0.928
V'=1	0	1	1	1
	1	0.8704	0.91	0.903
	2	1.184	1.32	1.291
V'=2	0	1	1	1
	0	1.198	1.28	1.251
	3	1.769	1.699	2.026
	4	2.925	3.756	3.487

DISCUSSION

The introduction of electronic transition moment factor has improved the agreement between theory and experiment, the nearer also is the approach of ratio δ smoothed to unity.

Robinson & Nicholls (1960) have obtained from their observations the relation

$$R_e(r) = \text{const.}\ (1 - 1.66r).$$

The value 1.66 of ρ, the coefficient in R_e - r relation, is significantly different from the present value of 0.4584. A check was made on their value by using their data. This gave the result as

$$R_e(r) = \text{const.}\ (1 - 0.3954r)$$

This value of ρ is very close to the value derived by the author. To have a further check on these ρ - values the smoothed transition probabilities using this coefficient in $R_e(r)$ variation are reduced and entered in table 2, column 5. The results show a better approach towards theoretical values by the use of coefficient 0.4583 than by the use of constant 0.3954.

Re-checking was made on Robinson & Nicholls value a number of times. It gave the same result for ρ, *i.e.* 0.3954. But it was difficult to trace the point at which the mistake has occured.

REFERENCES

Bates, 1949 *Proc. Roy. Soc.* A **196**, 217.

Elliot 1933 *Proc. Phys. Soc.* **45**, 627.

Nicholls & Jarmain, 1956 *Proc. Phys. Soc.* A **69**, 253.

Robinson & Nicholls, 1960 *Proc. Phys. Soc.* A **75**, 486.